

# Intrinsic electron-doping in nominal “non-doped” superconducting $(\text{La}, \text{Y})_2\text{CuO}_4$ thin films grown by dc magnetron sputtering

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The superconducting nominal “non-doped”  $\text{La}_{1.85}\text{Y}_{0.15}\text{CuO}_4$  (LYCO) thin films are successfully prepared by dc magnetron-sputtering and *in situ* post-annealing in vacuum. The best  $T_{\text{c0}}$  more than 13K is achieved in the optimal LYCO films with highly pure c-axis oriented T'-type structure. In the normal state, the quasi-quadratic temperature dependence of resistivity, the negative Hall coefficient and effect of oxygen content in the films are quite similar to the typical Ce-doped n-type cuprates, suggesting that T'-LYCO shows the electron-doping nature like known n-type cuprates, and is not a band superconductor as proposed previously. The charge carriers are considered to be induced by oxygen deficiency.

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## I. INTRODUCTION

Although the intense research since the discovery of high-temperature superconductors by Bednorz and Müller in 1986[1], the underlying mechanism for high temperature superconductivity remains elusive. It is well known that the parent compounds of all the high-temperature superconductors are antiferromagnetic half-filled Mott insulators in which the strong electronic correlation exists. Upon increasing doping holes or electrons to  $\text{CuO}_2$  sheets, the long-range antiferromagnetism is destroyed and superconductivity can be induced at the certain doping levels.

However, the new class of T'-structure cuprate superconductors, recently discovered by NTT research group, are nominal “non-doped” T'-(La, RE) $_2\text{CuO}_4$  (RE = Sm, Eu, Gd, Tb, Lu, and Y). RE is the isovalent cation with La and don't provide necessary charge carriers to  $\text{CuO}_2$  planes. They claimed that oxygen deficiencies can't afford a main source of charge carriers and these new superconductors are most plausibly so-called “band superconductors” [2, 3]. But they lacked further investigation on physical properties of these new class of superconductors. Furthermore, no other group can reproduce their work and acquire superconducting samples. Only one unsuccessful attempt was reported recently [4]. It is urgent to confirm these results at present.

According to our experimental experiences in the synthesis of La-based 214 cuprate films such as  $\text{La}_{2-x}\text{Ce}_x\text{CuO}_4$  (LCCO) films by sputtering and pulsed laser deposition (PLD) in the last several years [5], we studied the La-Y-Cu-O system. In this paper, we report the successful growth of the superconducting T'-LYCO films by dc magnetron sputtering. The behaviors of resistivity and Hall effect are investigated to disclose the nature of charge carriers in T'-LYCO.

## II. EXPERIMENT DETAILS

The  $\text{La}_{1.85}\text{Y}_{0.15}\text{CuO}_4$  (LYCO) films were fabricated by on-axis dc magnetron sputtering using a stoichiometric ceramic target. The target was synthesized by conventional solid state reaction. The appropriate powders of  $\text{La}_2\text{O}_3$ ,  $\text{Y}_2\text{O}_3$  and  $\text{CuO}$  of high purity with the composition ratio of cation La: Y: Cu=1.85:0.15:1.0, were mixed, grounded and sintered in air at 980°C for 48 hours with several intermediate regrindings. The calcined powder was then pressed into a 5 mm-thick disk with 50mm in diameter and was sintered at 1050°C for 24 hours.

The (100)-cut  $\text{SrTiO}_3$  ( $d=3.905\text{\AA}$ ) and LSAT [ $(\text{LaAlO}_3)_{0.3}(\text{Sr}_2\text{AlTaO}_6)_{0.7}$ ] ( $d=3.868\text{\AA}$ ) were used as substrates for deposition of LYCO films. The substrates were fixed to the heater which was located right above the target at a height of 35mm. The base pressure of the chamber prior to deposition was below  $5 \times 10^{-4}\text{Pa}$ . The sputtering gas was pure argon, and the pressure in the chamber was kept at about 60Pa during the deposition. Subsequently, LYCO was deposited at the temperature  $T_D = 600\text{--}755^\circ\text{C}$ . After deposition, the samples were first slowly cooled down to  $T_A = 600^\circ\text{C}$  in high vacuum (below  $10^{-4}\text{Pa}$ ), then annealed at this temperature for 15-30 minutes to remove the excess apical oxygen and finally followed by very slow cooling to room temperature in high vacuum. usually 15 minute's annealing in high vacuum is enough and longer annealing have no improving effect on the superconducting properties of the LYCO films. During the deposition, the sputtering current was ordinarily kept at about 200mA and the typical film thickness is around 3000Å after one hour's deposition. For these films thicker than 2500Å, there is no distinct difference on the transport properties of these films grown on whether STO or LSAT substrates in our experiments.

All the films are characterized by an x-ray diffractometer (Panalytical, X'pert Pro), using  $\text{Cu K}\alpha$  radiation. Their surface morphology and thickness are observed using an atomic force microscope (AFM, Digital Instru-

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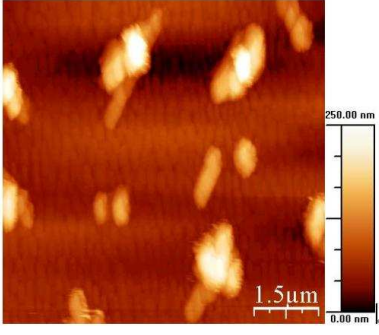


FIG. 3: Typical AFM image of the LYCO thin film deposited on the STO substrate at 690°C.

flection of the optimal films is only  $0.28^\circ$ , which confirms the good epitaxial growth of these films.

The surface morphology of typical films, studied by AFM, are shown in Fig. 3. Although the highly pure c-axis oriented T'-structure in the LYCO films has been confirmed by x-ray analysis, some randomly distributed particles on the film surface can be observed. The similar particles were also observed in the LCCO films grown by magnetron sputtering, which were considered mainly cuprous oxide  $\text{Cu}_2\text{O}$  [8]. Excessive Cu element in the films exists in the form of  $\text{CuO}_x$  particles, which suggest that there exists preferential sputtering during the deposition process. The higher deposition temperature help to crystallize these amorphous oxide particles and make them detectable by x-ray diffraction, as shown in Fig. 2(a). According to our experiences in the previous transport measurements in LCCO film prepared by magnetron sputtering, we believe that these  $\text{CuO}_x$  particles on the surface have no observable effect on the transport properties of the films.

The films in Fig. 4(a) are deposited at higher  $T_D$ , in which highly insulating T-phase co-exists as an impurity with superconducting T'-phase component. The coexistence leads to the partial superconducting (SC) transition (caused by the T'-phase component) appended to the whole insulating background (by the T-phase one). Upon increasing  $T_D$ , the proportion of the T'-214 component reduces and the SC transition weakens, shifting to lower temperature at the same time as shown in the inset of Fig. 4(a).

The films in Fig. 4(b) are deposited at lower  $T_D$ . As  $T_D$  decreases farther, the (110) component develops from the c-axis oriented optimal films, and becomes dominant near  $T_D=600^\circ\text{C}$ , which has been shown in Fig. 2(e). The (110) component introduces the contribution of out-of-plane transport to the whole  $\rho - T$  behavior of T'-LYCO films. On the other hand, lower deposition temperature rather strongly hinders the crystallization process and make deoxygenation in vacuum more difficult. At present, we cannot extract  $\rho_c$  and  $\rho_{ab}$  quantitatively from our results because poor crystallization and grain boundary existing in films deposited at low  $T_D$ . As

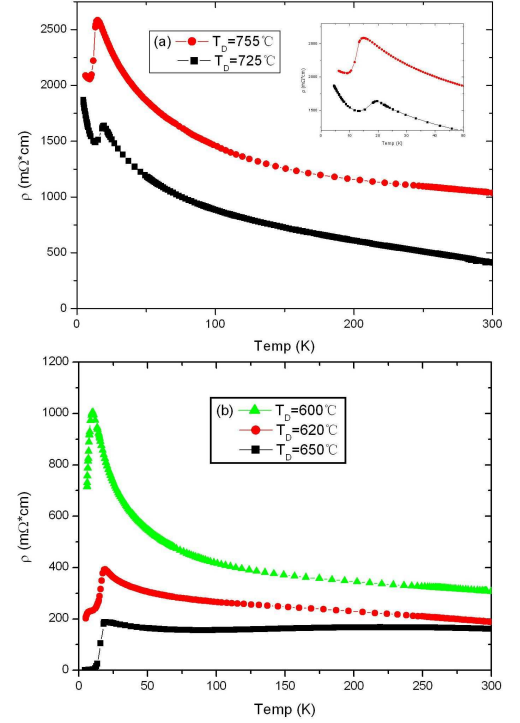


FIG. 4: The temperature dependence of the resistivity  $\rho$  of films deposited at different  $T_D$ : (a)  $755^\circ\text{C}$ ,  $725^\circ\text{C}$ ; (b)  $650^\circ\text{C}$ ,  $620^\circ\text{C}$ ,  $600^\circ\text{C}$ . The inset in (a) shows superconducting transitions in detail.

$T_D$  decreases, the influence of both unremoval of apical oxygen and grain boundary lead to the larger resistivity above  $T_C$  and more incomplete SC transition as well. It is possible that the semiconducting nature in normal state could arise from the contribution of out-of-plane resistivity. Similar results are reported in the study on the anisotropy of  $\text{Nd}_{2-x}\text{Ce}_x\text{CuO}_4$  (NCCO) through the films with different orientations [9].

For the optimal T'-214 films deposited at  $690^\circ\text{C}$ , the temperature dependence of the resistivity is shown in Fig. 5 (a). The  $T_{C0} = 13.5\text{K}$  and the width of SC transition less than  $1.5\text{K}$  (10-90% criterion) were acquired. The optimal film shows a metallic behavior in the whole range above  $T_C$  except for a slight upturn approaching  $T_C$  when  $T < T_{min} \sim 50\text{K}$ . In contrast to the well-known linear temperature dependence in the hole-doped cuprates like YBCO, the nearly quadratic dependence of  $\rho$  in the normal state is observed. This kind of behavior is similar to those observed in the electron-doped cuprates around optimal doping, such as  $\text{Ln}_{2-x}\text{Ce}_x\text{CuO}_4$  ( $\text{Ln}=\text{La, Pr, Nd, and Sm}$ ) [10, 11, 12, 13]. Now most researchers consider it as a Landau-Fermi liquid behavior due to electron-electron scattering.

The rigid formula for two-dimensional Landau-Fermi liquid

$$\rho(T) = \rho_0 + A(T/T_F)^2 \ln(T/T_F). \quad (1)$$

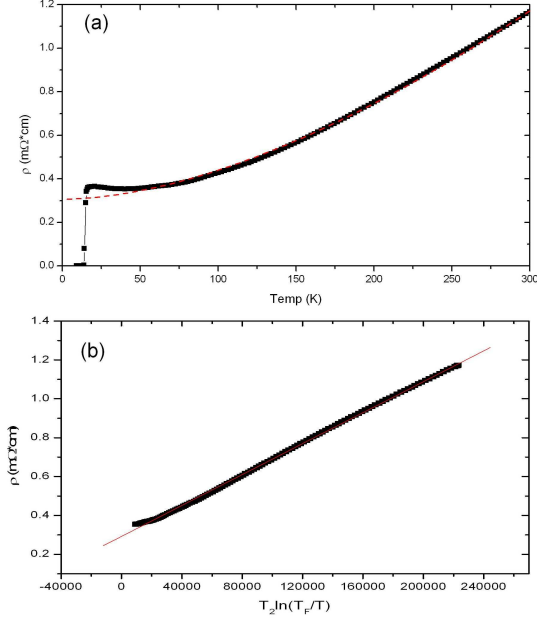


FIG. 5: Temperature dependence of resistivity for optimal c-axis oriented T'-LYCO films. (a)  $\rho$  vs.  $T$ , the dashed line is the fit to the formula (1); (b)  $\rho$  vs.  $T^2 \ln(T/T_F)$ .  $T_F = 5000\text{K}$  is used and the straight in (b) line is a guide to eyes.

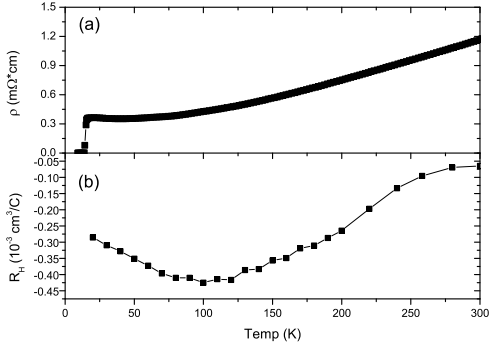


FIG. 6: Temperature dependence of the resistivity  $\rho$  (a) and Hall coefficient  $R_H$  (b) of the optimal film deposited at  $T_D=690^\circ\text{C}$ .

is used to fit the data. Where  $T_F$  is the Fermi temperature (we take  $T_F=5000\text{K}$  here) and  $\rho_0$  residual resistivity [14]. In the normal state the fitting is quite good above  $T_{min}$ , which is further confirmed by the fine linearity in the plot of in Fig. 5(b). The quadratic temperature dependence with logarithmic correction have been also observed in other electron-doped cuprates [15], which suggest the T'-LYCO may intrinsically be a typical electron-doped cuprate.

To clarify the origin of charge carriers, Hall coefficient  $R_H$  of the optimal films was measured as shown in Fig. 6. The negative  $R_H$  in normal states confirms the intrinsic electron-doped nature in T'-214 LYCO films. The  $R_H$

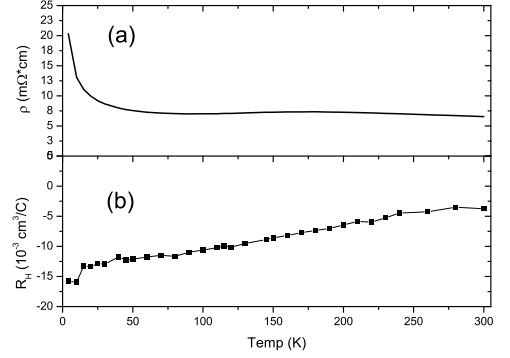


FIG. 7: Temperature dependence of the resistivity  $\rho$  (a) and Hall coefficient  $R_H$  (b) of the LYCO film that was deposited at  $T_D=690^\circ\text{C}$  and annealed at lower vacuum.

decreases gradually as temperature cooling from room temperature down to about 100K. Upon decreasing temperature further, a slight upturn toward to zero occurs. This kind of behavior is quite similar with other electron-doped cuprates as NCCO [16] and PCCO[12] at slightly less optimal doping level.

Till now, we cannot observe any prominent difference in T'-LYCO from the Ce-doped T'-214 cuprate superconductors. Since  $\text{Y}^{3+}$  and  $\text{La}^{3+}$  are isovalent in T'-LYCO, no net charge can be provided by doped  $\text{Y}^{+3}$ . The most probable origin of charge carriers is from oxygen deficiency since the superconductivity of our films can only be acquired by annealing in high vacuum.

At present, there is no way to determine the oxygen content in thin films accurately and straightforwardly. To confirm our assumption, we deposited LYCO films at the optimal temperature ( $T_D=690^\circ\text{C}$ ) but annealing them in lower vacuum ( $P_{O_2} \sim 0.6 \times 10^{-2}\text{Pa}$ ) by tuning the slide valve at the front end of the molecular pump. These films are still of pure T'-214 phase, but with less oxygen deficiency.

Their resistivity are much larger than the previous optimal films annealing in high vacuum ( $P < 1.0 \times 10^{-4}\text{Pa}$ ). At low temperature the insulating behavior is observed, and no superconductivity is found down to 4 K as shown in Fig. 7(a). The Hall coefficient  $R_H$  was also investigated as shown in Fig. 7(b).  $R_H$  is negative in the whole temperature range and decreases with decreasing temperature. The absolute value of  $R_H$  is much larger than that for optimal films, indicating less effective carrier density and being consistent with larger resistivity. This oxygen dependence of Hall behavior has been observed in  $\text{Nd}_{1.85}\text{Ce}_{0.15}\text{CuO}_{4-\delta}$  films by varying oxygen content [17]. Because the limit of vacuum that the sputtering chamber can reach is lower than that of the MBE chamber in the NTT group ( $P_{O_2} < 10^{-8} \text{ Torr}$ ) [2, 3]. Tuning the films to the overdoped region in the phase diagram cannot be performed by introducing more oxygen deficiency currently.

#### IV. CONCLUSIONS

We have successfully synthesized the superconducting T'-phase LYCO films by dc magnetron sputtering. The optimal growth conditions are explored in detail. The appropriate deposition temperature and succedent *in situ* annealing in high vacuum are the most crucial to acquire superconducting films with pure c-axis orientation. The optimal  $T_C$  of our samples is lower than the reported MBE-grown films (above 20K) at present. The biggest restriction to improve  $T_C$  is the limit of vacuum one can achieve. Detailed studies on the resistivity and Hall coefficient on T'-LYCO films, suggesting that this kind of so-called "non-doped" superconductor is intrinsically electron-doped cuprates. No exciting prominent difference in T'-LYCO from the well-known Ce-doped T'-214 cuprate superconductors(as LCCO, NCCO and PCCO) is observed in experiments. The charge carriers are the most likely from severe oxygen deficiency. But besides reducing  $t$  factor to improving the stability of T'-structure slightly, the role of  $Y^{3+}$  ion in superconducting

T'-LYCO is still elusive now. We have prepared Y-doped T'-  $Nd_2CuO_4$  and  $Pr_2CuO_4$  in films and bulk forms, in which there is no need for  $Y^{3+}$  ions to stabilize T'-214 structure. But no superconductivity is observed [18]. We suppose that the cooperation of large-sized  $La^{3+}$  ions with smaller  $Y^{3+}$  may enable the sufficient deficiency of oxygen in T'-structure to induce superconductivity. Further studies on the T'-LYCO films at various Y-doping levels and the in-plane substitution effect by magnetic or non-magnetic impurities are currently in process.

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